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# Partial collapse of the marine carbon pump after the Cretaceous–Paleogene boundary

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## ABSTRACT

The impact of an asteroid at the end of the Cretaceous caused mass extinctions in the oceans. A rapid collapse in surface to deep-ocean carbon isotope gradients suggests that transfer of organic matter to the deep sea via the biological pump was severely perturbed. However, this view has been challenged by the survival of deep-sea benthic organisms dependent on surface-derived food and uncertainties regarding isotopic fractionation in planktic foraminifera used as tracers. Here we present new stable carbon ( $\delta^{13}\text{C}$ ) and oxygen ( $\delta^{18}\text{O}$ ) isotope data measured on carefully selected planktic and benthic foraminifera from an orbitally dated deep-sea sequence in the southeast Atlantic. Our approach uniquely combines  $\delta^{18}\text{O}$  evidence for habitat depth of foraminiferal tracer species with species-specific  $\delta^{13}\text{C}$  eco-adjustments, and compares isotopic patterns with corresponding benthic assemblage data. Our results show that changes in ocean circulation and foraminiferal vital effects contribute to but cannot explain all of the observed collapse in surface to deep-ocean foraminiferal  $\delta^{13}\text{C}$  gradient. We conclude that the biological pump was weakened as a consequence of marine extinctions, but less severely and for a shorter duration (maximum of 1.77 m.y.) than has previously been suggested.

## INTRODUCTION

The Cretaceous–Paleogene (K–Pg, 66.02 Ma) boundary is defined by a major mass extinction of terrestrial and marine life (Schulte et al., 2010). One indication of the impact on marine life is the reduction, or reversal in some locations, of vertical marine carbon isotope gradients ( $\Delta\delta^{13}\text{C}$ ) between planktic and benthic species  $\delta^{13}\text{C}$ , for as long as 3 m.y. (D'Hondt et al., 1998). This has been interpreted as a global reduction in the export of organic matter sinking to deep water in the post-extinction ocean, i.e., weakening of the marine biological carbon pump (Zachos et al., 1989; D'Hondt et al., 1998; Coxall et al., 2006; Esmeray-Senlet et al., 2015). However, the lack of significant extinction of benthic foraminifera that depend on delivery of organic matter to the deep sea, and only relatively brief periods of change in their community structure (Alegret and Thomas, 2007, 2009; Thomas, 2007), has led some to challenge the idea of a large-scale prolonged (~3 m.y.) period of reduced carbon export (Culver, 2003; Alegret and Thomas, 2009). Analyzing isotopic patterns across this extinction event using depth-stratified foraminifera has special challenges: (1) the planktic foraminifera used as dissolved inorganic carbon (DIC) tracers are mostly lost to extinction (>90% taxonomic loss of Smit, 1982), such that no continuous single-species planktic  $\delta^{13}\text{C}$  record crossing the K–Pg boundary has been generated; (2) the new species that evolved in the aftermath are typically small and have strong  $\delta^{13}\text{C}$  vital effects resulting in test calcite that deviates from the DIC  $\delta^{13}\text{C}$  (Alegret and Thomas, 2009); and (3) there may

have been changes in ocean circulation patterns across the K–Pg boundary (Alegret and Thomas, 2009; Hull and Norris, 2011; MacLeod et al., 2011), which could have affected the foraminiferal  $\delta^{13}\text{C}$  signal.

To overcome these issues we have generated an open ocean record with robust dating, based on a firm understanding of paleoecology of the rapidly evolving post-extinction planktic taxa. The subsequent multispecies isotopic record improves estimates of vertical  $\delta^{13}\text{C}$  changes and provide more robust constraints on the magnitude and duration of the K–Pg ocean carbon system perturbation. A comparison of our data with benthic assemblage records for the first time reveals commonalities between proxy observations that help harmonize perspectives on the pelagic ecosystem response.

## MATERIALS AND METHODS

The K–Pg boundary event is captured in Ocean Drilling Program Site 1262 (Walvis Ridge; 27°11.15'S, 1°34.62'E; Fig. DR1 in the GSA Data Repository<sup>1</sup>). The K–Pg boundary occurs at ~216.6 m composite depth, calibrated to 66.02 Ma on an astronomically tuned time scale (Dinarès-Turell et al., 2014). We measured  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  on 10 species of planktic and 1 benthic foraminifera using a Thermo Finnigan MAT252 mass spectrometer equipped with an automated KIEL III carbonate preparation unit at Cardiff University, UK. Stable isotope results were calibrated to the Vienna Pee Dee belemnite (VPDB) scale by international standard NBS19 and analytical precision was better than  $\pm 0.05\text{‰}$  for  $\delta^{18}\text{O}$  and  $\pm 0.03\text{‰}$  for  $\delta^{13}\text{C}$ .

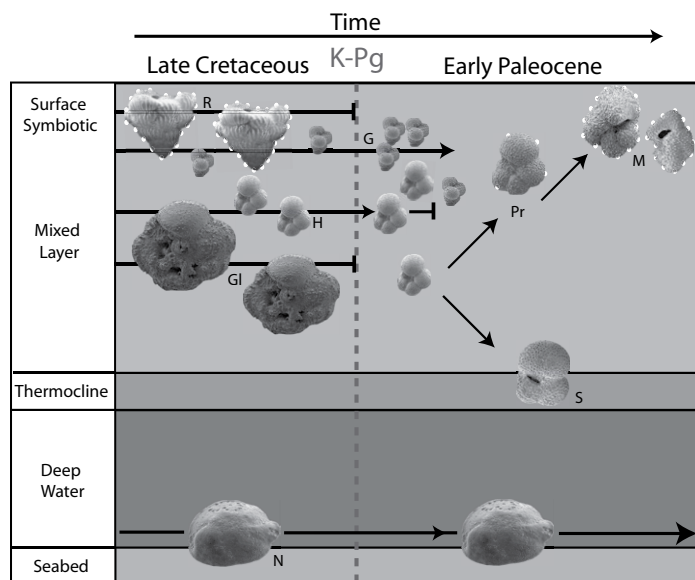
The selection of species was guided by previous work on early Paleocene planktic foraminifera isotopic depth ecologies (Birch et al., 2012) (Fig. 1): thermocline dwellers—*Subbotina trivalis* to *S. triloculinoidea*; mixed-layer dwellers—*Praemurica taurica* to *Pr. Inconstans*; and surface symbiotic—*Morozovella praeangulata* to *M. angulata* for downhole isotopic comparison. To establish a pre-extinction baseline of water column  $\Delta\delta^{13}\text{C}$  for the Cretaceous, *Globotruncana falsostuarta* and *Racemiguembellina fruticosa* were chosen as mixed-layer dwellers and surface symbiotic, respectively (Houston and Huber, 1998). The benthic species *Nuttallides truempyi* was picked to record  $\delta^{13}\text{C}$  of bottom water DIC because the species is considered to be in isotopic equilibrium with bottom waters (Shackleton et al., 1984). *Guembelitra cretacea* and *Hedbergella holmdelensis* were picked as the only mixed-layer dwelling species to range above the K–Pg boundary. Taxonomy follows Olsson et al. (1999) for the Paleocene and Bolli et al. (1985) for the Cretaceous.

## Planktic Foraminifera $\delta^{13}\text{C}$ Adjustment Factors

Special challenges to reconstructing K–Pg upper ocean  $\delta^{13}\text{C}$  arise due to the initial dominance of small (<150  $\mu\text{m}$ ) post-extinction opportunists

<sup>1</sup>GSA Data Repository item 2016088, location figure, further details of  $\delta^{13}\text{C}$  adjustment values with figure, and raw isotope data, is available online at [www.geosociety.org/pubs/ft2016.htm](http://www.geosociety.org/pubs/ft2016.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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**Figure 1.** Changing ecology schematic of selected foraminiferal species for isotopic analysis across the Cretaceous-Paleogene (K-Pg) boundary. White circles indicate photosymbionts. M—*Morozovella angulata*, Pr—*Praemurica inconstans*, S—*Subbotina triloculinoidea*, N—*Nuttallides trempyi*, R—*Racemiguembelina fructicoa*, Gl—*Globotruncana falsostuarta*, G—*Guembelitra cretacea*, H—*Hedbergella holmdelensis*.

and subsequent re-evolution of photosymbiotic foraminifera (Fig. 1); both ecologies are associated with distinct fractionation effects causing test calcite  $\delta^{13}\text{C}$  to be depleted or enriched, respectively, relative to ambient DIC  $\delta^{13}\text{C}$  values (D'Hondt and Zachos, 1993; Birch et al., 2012, 2013). Small test size has been linked with a relatively larger proportion of respired (metabolic)  $^{12}\text{C}$  being incorporated into the test calcite, resulting in offsets from inferred DIC  $\delta^{13}\text{C}$  of 0.3‰–2‰. Conversely, high  $\delta^{13}\text{C}$  (as much as 1.5‰ greater than other inferred surface taxa) and positive  $\delta^{13}\text{C}$ -size signatures typify photosymbiotic species, including *Praemurica* and *Morozovella*, which acquired this ecology at ca. 63.5 Ma (Fig. 2; Birch et al., 2012). The net effect of these diverging vital effects would be to compress the  $\delta^{13}\text{C}$  gradient just after the boundary (as photosymbiotic and large forms were lost) and exaggerate its recovery. To account for these effects we experimented with applying isotopic ecoadjustment factors (see the Data Repository).

## RESULTS

### Carbon Isotope Record

The  $\delta^{13}\text{C}$  data from late Maastrichtian planktic and benthic foraminifera show offsets between ~1‰ and ~2.1‰ (for asymbiotic and symbiotic, respectively). At the K-Pg boundary the  $\delta^{13}\text{C}$  values converge, largely due to a reduction in the planktic  $\delta^{13}\text{C}$  (Fig. 2). The first measurement in surviving *H. holmdelensis* after the K-Pg boundary shows a decrease by ~1‰, while benthic  $\delta^{13}\text{C}$  values hardly change (Fig. 2).  $\delta^{13}\text{C}$  of *G. cretacea* decreases only slightly across the K-Pg boundary and is unusually depleted compared to other species, consistent with its small size (Birch et al., 2012).

The pattern of post K-Pg boundary  $\Delta\delta^{13}\text{C}$  (unadjusted) can be divided into three stages (Figs. 2A, 2C). An initial stage (stage 1), from the K-Pg boundary to ~300 k.y., is characterized by planktic to benthic  $\Delta\delta^{13}\text{C}$  values that are close to zero or negative and very low bulk  $\delta^{13}\text{C}$  and carbonate accumulation rates. In stage 2, planktic-benthic  $\Delta\delta^{13}\text{C}$  began to return to pre-extinction levels and bulk  $\delta^{13}\text{C}$  and carbonate accumulation rates also increased.  $\Delta\delta^{13}\text{C}$  increased gradually from ~0.4‰, approaching the pre-extinction surface to deep  $\Delta\delta^{13}\text{C}$  of ~1.0‰ ~1.77 m.y. after the event. The final stage (stage 3) of recovery, ~2.5 m.y. after the event, marks

the return of differences between mixed-layer and thermocline planktic foraminifera. The application of ecoadjustment factors (Fig. 2E), which take into account the effect of  $^{12}\text{C}$  enrichment in small species, shows no obvious reversal in the  $\delta^{13}\text{C}$  gradient.

### Oxygen Isotope Record

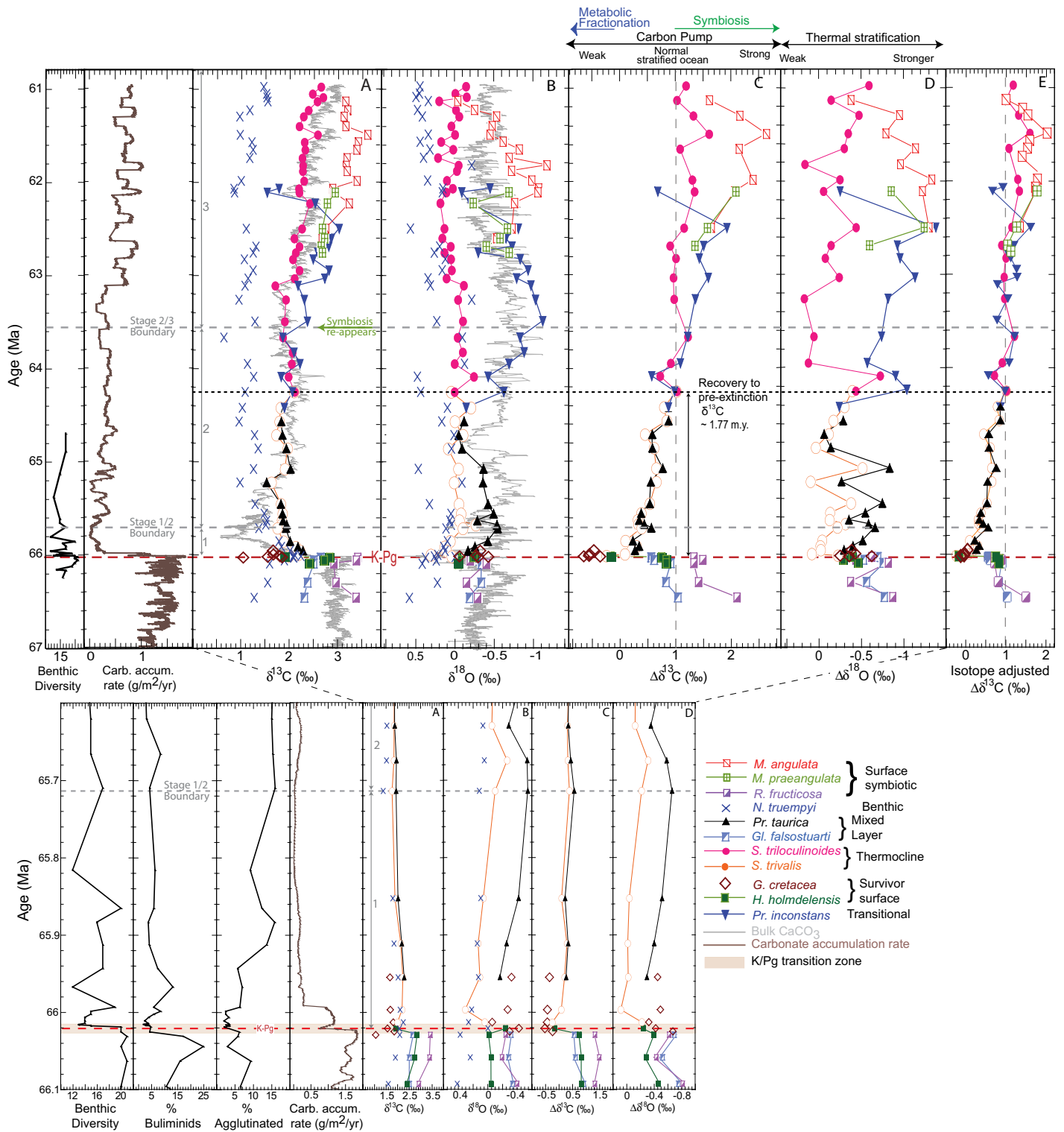
$\delta^{18}\text{O}$  data provide critical evidence for habitat depth of planktic foraminiferal species, a constraint that was not taken into account by previous studies of the  $\delta^{13}\text{C}$  gradient (D'Hondt et al., 1998). The species-specific  $\delta^{18}\text{O}$  (Fig. 2) data indicate a thermally stratified water column during the late Maastrichtian. A brief (~10 k.y.) warming is indicated by an ~0.24‰ decrease in  $\delta^{18}\text{O}$  of *H. holmdelensis* and *N. trempyi* at the K-Pg boundary. Benthic mixed-layer  $\Delta\delta^{18}\text{O}$  decreased but, importantly, benthic thermocline  $\delta^{18}\text{O}$  values converge for ~300 k.y. after the K-Pg boundary. Bulk carbonate  $\delta^{18}\text{O}$  shows an increase from ca. 66.2 Ma, with highest values at the boundary, but this trend is not echoed by the foraminifera, although the resolution difference between bulk and foraminifera records may account for this. Bulk  $\delta^{18}\text{O}$  values subsequently decrease and generally follow the surface mixed-layer planktic foraminifera.

## DISCUSSION

The new records presented here reveal the importance of understanding and controlling the paleoecological effects of the analyzed species when interpreting the  $\delta^{13}\text{C}$  signal. Our records suggest that carbon export started to recover ~300 k.y. after the K-Pg boundary, with pre-extinction values restored by ca. 64.25 Ma, i.e., ~1.77 m.y. after the event, rather than 3 m.y., as suggested previously (D'Hondt et al., 1998). This recovery process was also not staggered; rather,  $\Delta\delta^{13}\text{C}$  values continued to steadily increase. The last stage of recovery, thought to mark the full recovery in  $\Delta\delta^{13}\text{C}$  in older records (D'Hondt et al., 1998; Coxall et al., 2006), coincides with the reacquisition of photosymbiosis (Norris, 1996; Birch et al., 2012) and likely reflects an artifact of paleoecological evolution, as the change occurs in the surface rather than the thermocline or benthic foraminifera.

Paleoceanographic changes could have affected  $\Delta\delta^{13}\text{C}$  and our interpretations. A change in water mass would affect  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . To ensure that our record is driven by export productivity changes, supported by a decrease in carbonate accumulation (Fig. 2) and not temperature and/or local water mass changes, we interrogate our  $\delta^{18}\text{O}$  record. Only the benthic and thermocline  $\delta^{18}\text{O}$  values converge at the boundary, suggesting a deepening of the thermocline, warming or change in the source and/or chemistry of bottom waters, and not surface waters. The timing of circulation changes, however, do not match  $\delta^{13}\text{C}$  decreases, as water mass changes are suggested to have started before the K-Pg boundary (Frank and Arthur, 1999; MacLeod et al., 2011). In addition, thermal stratification persisted between the surface and deep ocean despite transitioning from Cretaceous to Paleocene taxa. Therefore, potential water mass changes could only partially explain the  $\Delta\delta^{13}\text{C}$  reduction, and a partial reduction in organic carbon export flux is still required. Geochemical models also support this interpretation, suggesting that a reduction of between 30% and 40% (depending on ocean basin; Ridgwell et al., 2010) in organic export or 10% in burial (Kump, 1991) is needed to achieve the surface to deep  $\Delta\delta^{13}\text{C}$  seen at the K-Pg boundary.

Spatial heterogeneity between the major ocean basins and shelf recovery patterns has been demonstrated (Hull and Norris, 2011; Sibert et al., 2014; Esmeray-Senlet et al., 2015), with Pacific Ocean sites (e.g., Shatsky Rise) often showing increases in export production after the boundary, while Atlantic and Indian Ocean sites (e.g., São Paulo, Walvis Ridge, and Wombat Plateau) show either no change or a decrease. Evidence suggests that a thermohaline circulation system similar to today was established in the Late Cretaceous (Frank and Arthur, 1999), which could result in regional differences, as suggested by Hull and Norris (2011). While this hypothesis would have been insufficient to explain a reduction for several million years, our newly constrained and significantly shorter timing makes this hypothesis more viable.



**Figure 2.** Benthic and planktic foraminiferal stable isotopes from Ocean Drilling Program (ODP) Site 1262, calibrated against Vienna Peedee belemnite (VPDB) and against the time scale of Dinares-Turell et al. (2014). A: Carbon ( $\delta^{13}\text{C}$ ) isotope. B: Oxygen ( $\delta^{18}\text{O}$ ) isotope. C: Carbon ( $\delta^{13}\text{C}$ ) isotope differences ( $\Delta$ ) between individual planktic and benthic foraminifera species. D: Carbon ( $\delta^{18}\text{O}$ ) isotope differences ( $\Delta$ ) between individual planktic and benthic foraminifera species. E: Adjustment option 2 (see the Data Repository [see footnote 1]). Bottom: Close-ups of the Cretaceous-Paleogene (K-Pg) boundary for A–D. Bulk isotope and carbonate accumulations (Carb. accum.) rate data are from Kroon et al. (2007) and benthic diversity data are from Alegret and Thomas (2007). K-Pg transition zone marks the lithologic change observed in the core. Genera abbreviations: M.—*Morozovella*, Pr.—*Praemurica*, S.—*Subbotina*, N.—*Nuttallides*, R.—*Racemiguembelina*, Gl.—*Globotruncana*, G.—*Guembelitra*, H.—*Hedbergella*.

The global survival of benthic foraminifera is compelling evidence that the food supply to the deep ocean never ended (Alegret and Thomas, 2009; Culver, 2003). Benthic foraminifera, which are associated with high food abundance (e.g., buliminids), declined and numbers remained low (Alegret and Thomas, 2007) after the K-Pg boundary. Diversity decreased and the community structure changed to smaller, agglutinated, opportunistic forms of benthic foraminifera (Alegret and Thomas, 2007, 2009). These major changes in benthic assemblages lasted for ~300 k.y., which closely matches our stage 1 (Fig. 2) of the carbon recovery, based on our independent  $\delta^{13}\text{C}$  record. The high variability in benthic community structure decreased and began to stabilize at the same time as interspecies  $\delta^{13}\text{C}$  differences between planktic and benthic foraminifera recovered.

## CONCLUSIONS

The  $\Delta\delta^{13}\text{C}$  collapse at the boundary is likely a combination of vital effects and a real reduction of the biological pump. Water mass changes may have had some influence, but the timing and dominance of deep rather than surface water changes make this unlikely. Initial larger scale changes to export production to ~300 k.y. after the K-Pg boundary are indicated by both the benthic foraminiferal assemblages and our  $\delta^{13}\text{C}$  data (stage 1). A gradient between surface and deep  $\delta^{13}\text{C}$  reappeared concomitantly with stabilization of the benthic assemblages.  $\Delta\delta^{13}\text{C}$  continued to increase until pre-extinction values were reached at 1.77 m.y. after the event, significantly earlier than has previously been suggested. The final stage of the  $\Delta\delta^{13}\text{C}$  recovery likely represents a vital effect and not a change in export production, as it is coincident with the first geochemical evidence of photosymbiosis in Paleocene taxa.

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